Chapter 3.1, Atomic wavefunction family album

We have learned for the one-dimensional examples of standing waves that the wavefunction for the lowest possible energy has one loop, that the wavefunction for the second lowest possible energy has two loops, and one loop is added for each higher energy.

Here is how to extend this idea of the number of loops reflecting relative energy to the three dimensional wavefunctions in atoms. First, because atoms are spherical, there will be separate sets of loops in the radial direction (going out from the nucleus) and in the angular directions (going around the nucleus at fixed distance from it). Second, because the angular wavefunction at $\phi = 0$ is the same as $\phi = 2\pi$, wavefunctions meet smoothly after one full cycle in ϕ. This means that the lowest energy angular variation must have one full wavelength (that is, two loops rather than one loop), and each increase in angular excitation must be accompanied by the addition of another full wavelength (two additional angular loops). Angular loops appear in the electron density as nodal planes through the nucleus.

We call the number of radial loops j and the number of angular wavelengths ℓ (the number of nodal planes).

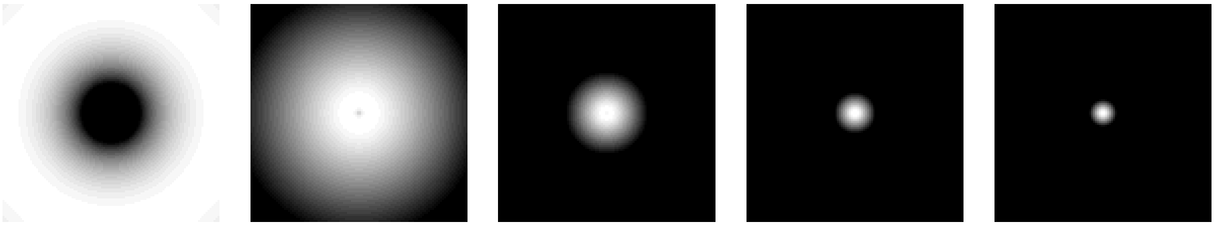
With this background, let's sort out atomic wavefunctions in families according to the number, ℓ, of wavelengths moving around the nucleus at fixed distance from it, and then, within a family, the according to the number, n, of loops moving radially outward from the nucleus.

In the displays below are shown the probability densities in the *xy* plane of the simplest members for the families of hydrogen atom wavefunctions with zero, one and two angular wavelengths.

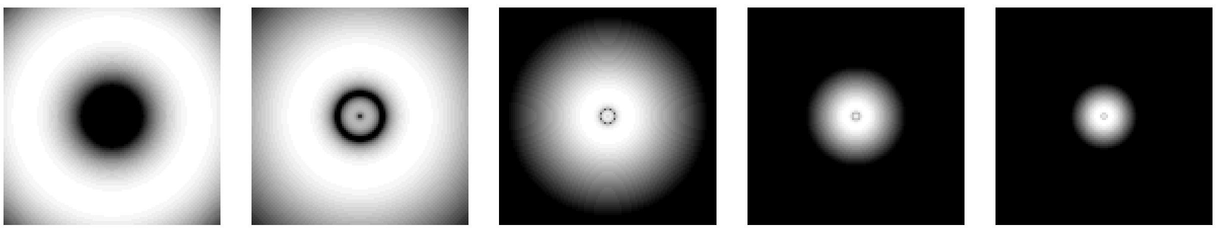
The displays consist of cross sections through the electron "cloud" of several members of each family. The nucleus is at the center of each cross section. Each cross section is displayed at five different scales (magnifications) . From left to right, the width and height are 1, 10, 30, 60 and 90 Å, that is, 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density. Since all of the displays at a given magnification are on the same scale, comparing displays of different orbitals makes it easy to compare their relative sizes.

■ Spherical (s) family

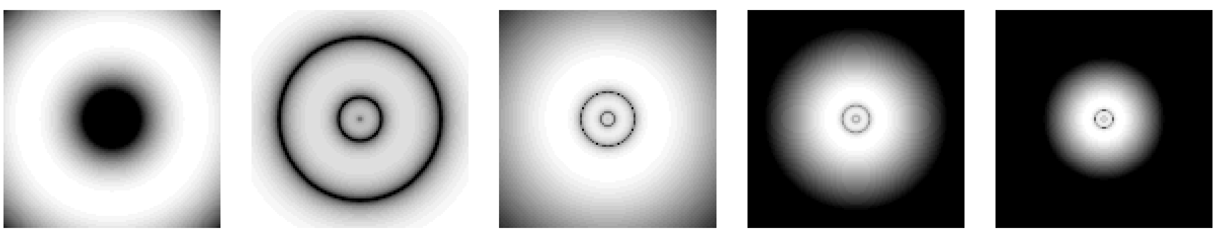
The members of the family of hydrogen atom wavefunctions with zero angular wavelengths (and with spherical symmetry) are call *s orbitals*. The lowest energy member, 1s, has one radial loop (moving out from the nucleus), the second lowest energy member, 2s, has two radial loops, etc.



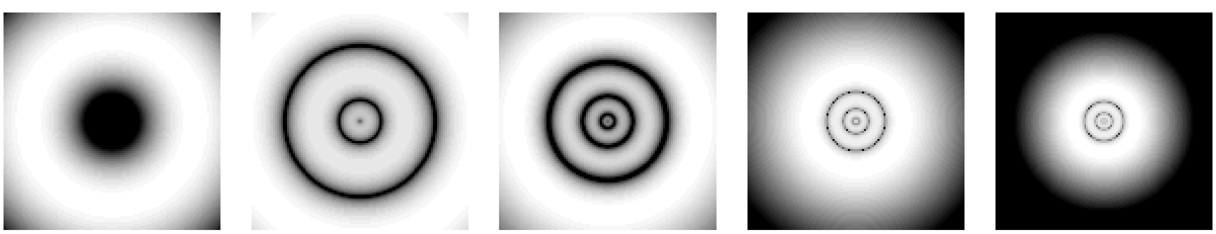
Probability density in the *xy* plane of the 1s hydrogen atom wavefunction. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.



Probability density in the *xy* plane of the 2s hydrogen atom wavefunction. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.



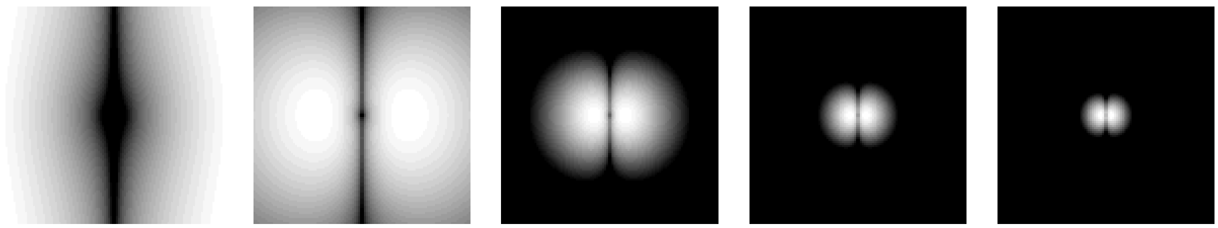
Probability density in the *xy* plane of the 3s hydrogen atom wavefunction. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.



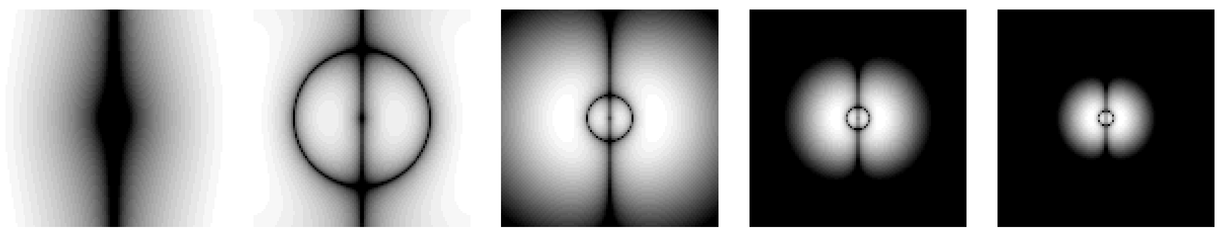
Probability density in the *xy* plane of the 4s hydrogen atom wavefunction. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.

■ Dumbbell (p) family

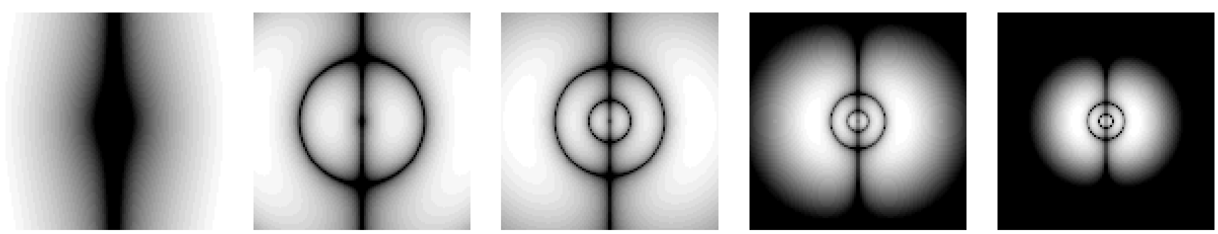
The members of the family of hydrogen atom wavefunctions with one angular wavelengths (and so one nodal plane through the nucleus) are call *p orbitals*. There are three different kinds p orbitals, differing by the axis along which the dumbbell shape is aligned. The three different kinds of p orbitals are called p_x, p_y, and p_z. The lowest energy members, the three 2p orbitals, each have one radial loop (moving out from the nucleus), the second lowest energy members, 3p, each have two radial loops, etc.



Probability density in the *xy* plane of the $2p_x$ hydrogen atom wavefunction. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.



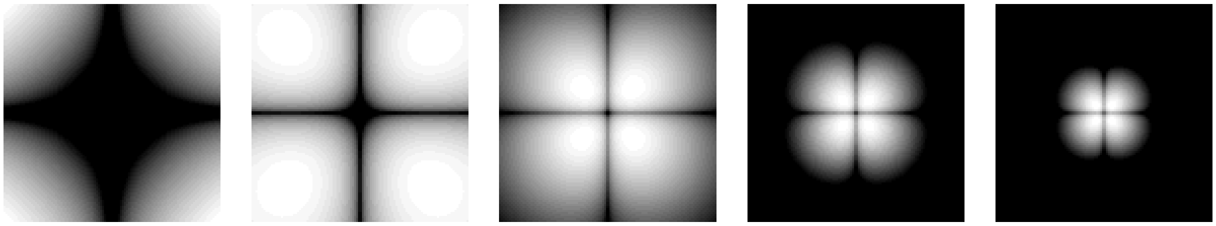
Probability density in the *xy* plane of the $3p_x$ hydrogen atom wavefunction. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.



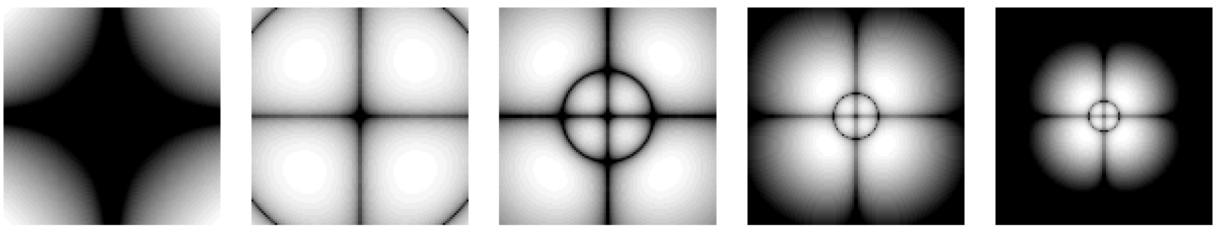
Probability density in the *xy* plane of the $4p_x$ hydrogen atom wavefunction. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.

■ Cloverleaf (d) family

The members of the family of hydrogen atom wavefunctions with two angular wavelengths (and so two nodal planes through the nucleus) are called *d orbitals*. There are five different kinds of d orbitals, differing by the orientation of the cloverleaf shape. The five different kinds of d orbitals are called d_{z^2}, d_{yz}, d_{zx}, d_{xy}, and $d_{x^2-y^2}$. The lowest energy members, the five 3d, each have one radial loop (moving out from the nucleus), the second lowest energy members, 4d, each have two radial loops, etc.



Probability density in the *xy* plane of the 3d_{xy} hydrogen atom wavefunction. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.



Probability density in the *xy* plane of the 4d_{xy} hydrogen atom wavefunction. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.

■ Grouping by relative energy

It turns out one-electron atom electron waves for which sum,

$$n = \text{radial loops} + \text{nodal planes},$$

is the same all have the same energy. The sum is called the principal quantum number, n, and the energy of a one-electron atom with nuclear charge $+Z\,e$ is

$$E_n = -13.6\,\text{eV}\,Z^2/n^2,$$

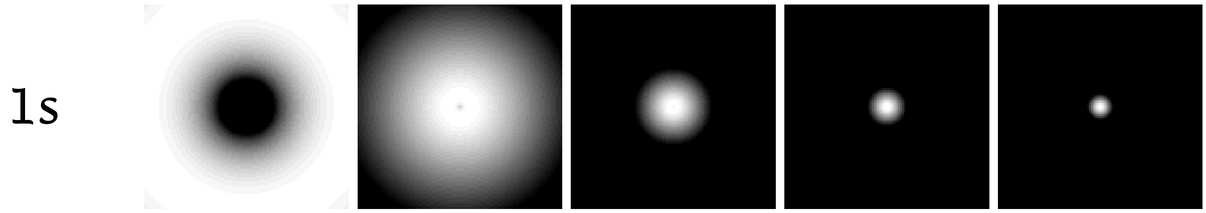
relative to the zero of energy being when the electron wave is first detached from the atom (corresponding to $n = \infty$). For hydrogen atom, $Z = 1$, and so the energies of the electron waves shown here are $E_n = -13.6\,\text{eV}/n^2$.

> Show that the ionization energy of an electron wave with principal quantum number n is $+13.6\,\text{eV}/n^2$. Hint: The ionization energy is , $E_\infty - E_n$.

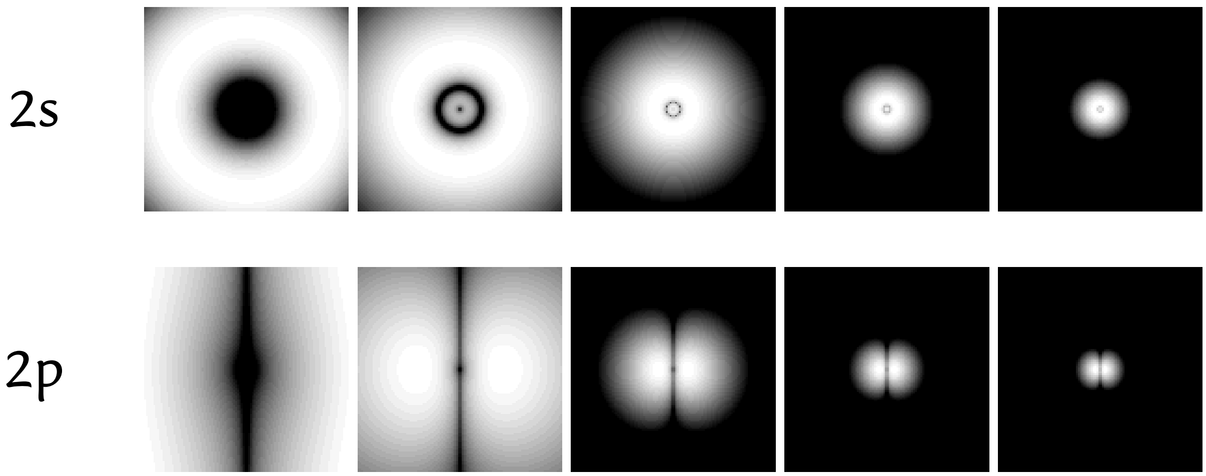
Since energy depends on principal quantum number, n, by convention family members are labelled by n rather than by the number of radial loops. For example,

- the lowest member of the s (spherical) family is called 1s, since it has one radial loop and zero nodal planes, and so $n = 1 + 0 = 1$;
- the lowest member of the p (dumbbell) family is called 2p, since it has one radial loop and one nodal plane, and so $n = 1 + 1 = 2$;
- the lowest member of the d (cloverleaf) family is called 3d, since it has one radial loop and two nodal planes, and so $n = 1 + 2 = 3$.

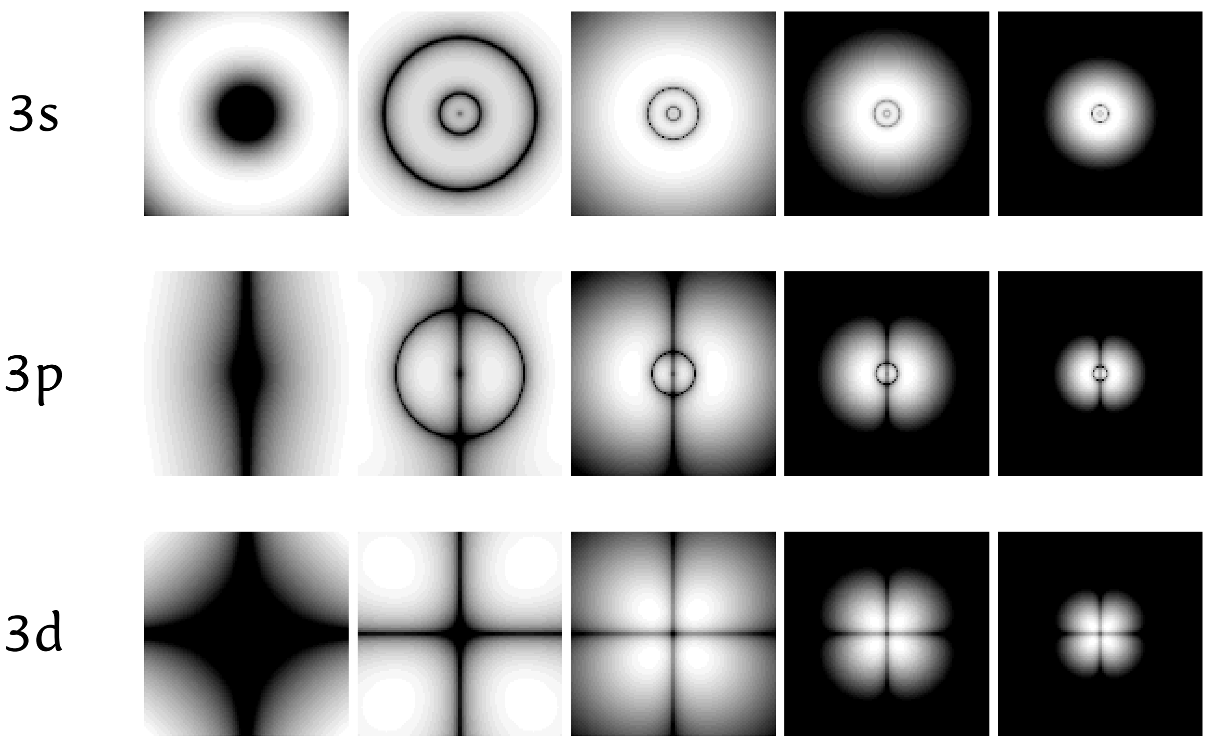
Here are the hydrogen atom electron clouds grouped by increasing principal quantum number, n, and so according to their relative energy.



Hydrogen atom n = radial loops + nodal planes = 1 family: 1s, energy −13.6 eV. Probability density in the xy plane. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.



Hydrogem atom n = radial loops + nodal planes = 2 family: 2s and 2p, energy $-13.6\text{ eV}/2^2 = -3.40$ eV. Probability density in the xy plane. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.



Hydrogen atom n = radial loops + nodal planes = 3 family: 3s, 3p, and 3d, energy $-13.6\text{ eV}/3^2 = -1.51$ eV. Probability density in the xy plane. The nucleus is at the center. From left to right, the width and height are 0.1, 1, 3, 6, and 9 nm. The brightness of the display is proportional to the probability density.

■ Questions

1. How does the relative size of the *n*s orbitals compare? Answer: Size increases with the number of radial loops, *j*.

2. Does the size of the *n*p and of the *n*d orbitals increase with *n*? Answer: Yes.

3. How does the relative size of the innermost loop of the *n*s orbitals compare? Answer: Excepting 1s, they are all about the *same* size.

4. How does the relative size of the innermost loop of the *n*p orbitals compare? Answer: Excepting 2p, they are all about the *same* size.

5. How does the relative size of the outermost loop of the *n*s orbitals compare? Answer: As *n* increases, the outermost loop *increases* in size.

6. How does the relative size of the outermost loop of the *n*p orbitals compare? Answer: As *n* increases, the outermost loop *increases* in size.

7. Which of the orbitals 4s, 4p, and 4d is the largest, that is, has the electron density distributed over the greatest volume? Answer: 4s.

8. Which of the orbitals 4s, 4p, and 4d is the smallest, that is, has the electron density distributed over the smallest volume? Answer: 4d.

9. Is the relative size ordering *n*s > *n*p > *n*d true for $n = 3$ as well? Answer: Yes.